Abstract No. Yu0133

Structure of Interfacial Liquids under Shear

C.-J Yu, G. Evmenenko, J. Kmetko, and P. Dutta (Northwestern U.)

Beamline(s): X18A

Introduction: Although anomalous shear response in nanoconfined Newtonian liquids has been observed and presumed to indicate changes in ordering [1-3], no direct structural evidence has been reported, mainly because of experimental difficulties in confining liquids on nanometer scale and probing the structure of liquids under shear at the same time. (Complex fluid structure has been observed to change at quite low shear rates, but the effects of shear on classical liquids are of more general significance.) We found a way to overcome the difficulties by designing a new X-ray cell. We have thereby been able to directly observe the effects of shear on interfacial liquid structure.

Methods and Materials: We designed a shear cell to observe molecular scale behavior of liquids under shear using X-ray reflectivity. The liquid under study is held between the kapton window and the silicon substrate while as shown in Fig. 1. Shear stress is applied by rotating the stainless steel housing and thus the kapton window. We used two types of Newtonian liquids: a non-entangling, spherical molecule tetrakis(2-ethylhexoxy)silane (TEHOS) and an entangling, linear polymeric molecule polydimethylsiloxane (PDMS, molecular weight ~5200, viscosity 100cSt, polydispersity 1.15, ~70 monomer units). For TEHOS, we applied shear for 1 minute, stopped shear, and measured the reflectivity at various distances from the center of the rotation, i.e. at regions with different shear rates. For PDMS, shear was applied for 1.5 minutes.

Results: Fig. 2 shows the progressive disruption of the diffraction peak from non-entangling TEHOS at the solid-liquid interface as the shear rate increases. We note that the position and width of the diffraction peak do not change significantly but the peak height does. To analyze the relation between the peak height and the shear rate, we fitted the data with a Gaussian peak and an exponentially decaying background. In Fig. 3, we plot the peak height against the shear rate (log-log plot). The data point from unsheared TEHOS cannot be shown in Fig. 3 because of the log scale, but is represented by the horizontal dashed line. The result is very similar to the viscosity change with respect to the shear rate for the Newtonian liquids confined between two mica surfaces separated by 3 to 10 molecule sizes [1]. They report a slope of about –2/3 (in a log-log plot) for dodecane and octamethylcyclotetrasiloxane, and as shown in Fig. 3, such a slope is consistent with our X-ray data as well. For entangling PDMS, we observed a very different structural behavior. Fig. 4(a) shows the reflectivity data for unsheared PDMS in our shear cell that is essentially the same as our previous report showing no diffraction peak due to layering [4]. We saw a change only at shear rates of ~$10^4 s^{-1}$. The subsequent reflectivity data shown in Fig. 4(b) indicates pronounced layering of PDMS molecules. The Patterson function of our data (inset of Fig. 4) shows that the density oscillations are confined near the interface. This layered PDMS relaxed back to the disordered state in ~3 hours, as indicated by the loss of peak intensity (Fig. 4(c,d)).

Conclusions: We observed that shear flow affects the interfacial structures of two liquids, TEHOS and PDMS, in different ways. In a liquid of 'spherical' molecules that order at the interface in the absence of shear, we see that flow reduces the ordered area, but it does not reduce the number of layers in regions that remain ordered. In a liquid of long flexible molecules, on the other hand, layering develops at high shear rates, a structural signal of shear-driven disentanglement.

Acknowledgments: This work was supported by the US National Science Foundation under grant no. DMR-9978597, and performed at the Materials Research Collaborative Access Team (Sector 10, Advanced Photon Source) and at MATRIX (Beam Line X-18A, National Synchrotron Light Source).

References:

[1]. H.-W. Hu, G. A. Carson, and S. Granick, "Relaxation time of confined liquids under shear," Phys. Rev. Lett. **66**, 2758 (1991).

[2]. B. V. Deryaguin, V. V. Karasev, I. A. Lavygin, I. I. Skorokhodov, and E. N. Khromova, "Boundary viscosity of polydimethylsiloxane liquids and their binary mixtures," Prog. Surf. Sci. **40**, 322 (1992)

[3]. S. Granick, H.-W. Hu, and G. A. Carson, "Nanorheology of confined polymer melts. 2. Nonlinear shear response at strongly adsorbing surfaces," Langmuir **10**, 3867 (1994)

[4]. G. Evmenenko, S. W. Dugan, J. Kmetko, and P. Dutta, "Molecular ordering in thin liquid films of polydimethylsiloxanes," Langmuir **17**,4021 (2001).

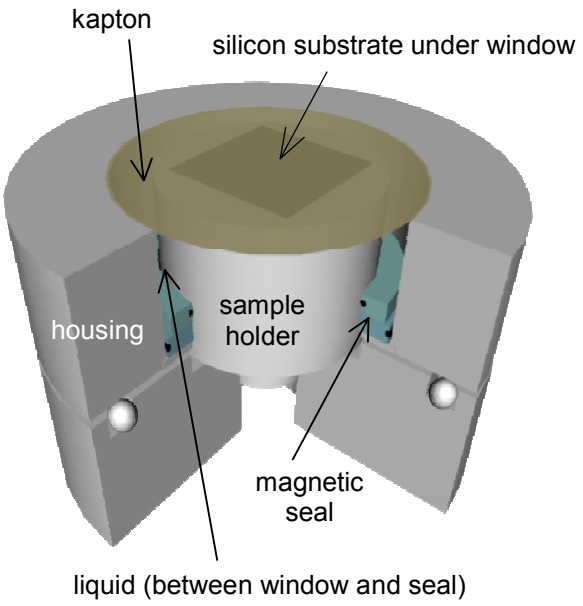

Figure 1: Schematic diagram of the experimental setup. The outer housing and attached kapton window are rotated to apply shear.

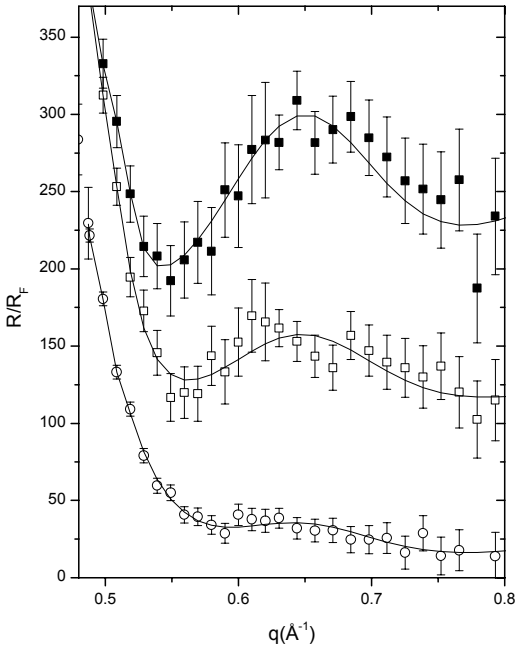

Figure 2: Normalized x-ray reflectivity data for ~13μm thick TEHOS film: unsheared (■); after rotational shear for one minute at the shear rate of 540 ± 40 s^{-1} (□) and 800 ± 40 s^{-1} (●). The scans are shifted vertically by arbitrary amounts for clarity.

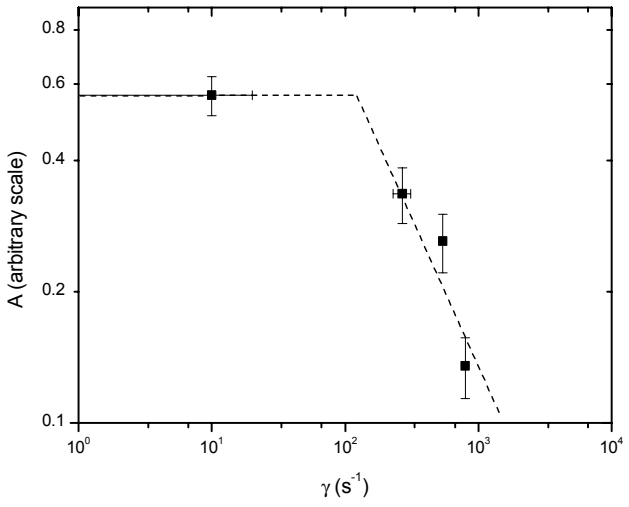

Figure 3: The height of the TEHOS diffraction peak (A) vs. shear rate (applied for 1 min) in a log-log plot. Beyond a threshold shear rate, the amplitude drops rapidly. The lines are guides to the eye; the slope of the line at right is –2/3.

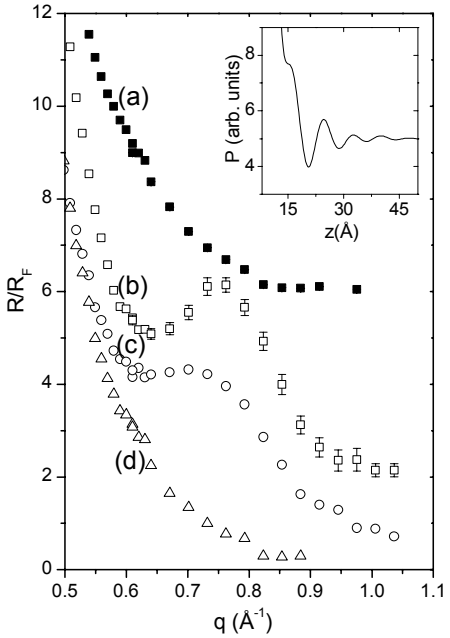

Figure 4: Normalized x-ray reflectivity data for a ~1μm thick PDMS film sheared for 1.5 minutes at a rate of $10^4 s^{-1}$. The scans were made (a) 0.5 hours (c) 1 hour (d) 3 hours after shear was applied. Scan (a) is from unsheared PDMS, for comparison. The scans are shifted vertically by arbitrary amounts for clarity.